Report for 2000WI8G: Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study

- Articles in Refereed Scientific Journals:
  - Hintelmann, H., R. Harris, A. Heyes, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S. Lindberg, J.W.M. Rudd, K.J. Scott and V.L. St. Louis. 2002. Reactivity and mobility of new and old mercury in a boreal forest ecosystem during the first year of the METAALICUS study. Environmental Science and Technology. 36(23):5034-5040.
  - Babiarz C.L, J.P. Hurley, D.P. Krabbenhoft, C.C. Gilmour, and B.A. Branfireun. 2003. Application of ultrafiltration and stable isotope amendments to the partitioning of mercury in lake water and over land runoff. Science of the Total Environment. 304: 295-303
  - Babiarz, C.L., J.P. Hurley, D.P. krabbenhoft, T.R. Trinko, M. Tate, S.P. Chadwick and D.E. Armstrong. 2003. A hypolimnetic mass balance of mercury from a dimictic lake: results from the METAALICUS project. Journal de physique IV. 107:83-86.
- Conference Proceedings:
  - Harris, R.C., J.W.M. Rudd, M. Amyot, C. Babiarz, K. Beaty, P. Blanchfield, A. (Drew) Bodaly, B. Branfireun, C.C. Gilmour, A. Heyes, H. Hintelmann, J. Hurley, C. Kelly, D. Krabbenhoft, S. Lindberg, M. Paterson, C. Podemski, K. Rolfhus, K. Sandilands, K. Scott, G. Southworth, V. St. Louis. 2001. METAALICUS: A Study to Determine the Relationship Between Mercury Deposition and MeHg Concentrations of Fish. Workshop on the Fate, Transport, and Transformation of Mercury in Aquatic and Terrestrial Environments Sponsored by the U.S. Environmental Protection Agency. West Palm Beach, Florida. May.
  - Hurley, J.P., M. Amyot, M., K. Beaty, K., P. Blanchfield, R.A. Bodaly, B. Branfireun,, C.Gilmour, R.C. Harris, A. Heyes, H. Hintelmann, C. Kelly, D. Krabbenhoft, S. Lindberg, M. Paterson, C. Podemski, J.W.M. Rudd, K. Sandilands, G. Southworth, V. St. Louis. 2003. Watershed-level Addition of Mercury Stable Isotopes: A Tool for Understanding Processes from Deposition to Bioaccumulation. Conference on Frontiers in Assessment Methods for the Environment (FAME). Minneapolis, MN. August. (Invited).
  - Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. An overview of the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States. American Water Resources Association. Minocqua, Wisconsin. February 27 & 28, 2003.
  - Babiarz, C., J. Hurley, D. Krabbenhoft, T. Trinko, M. Tate, S. Chadwick, and D. Armstrong. A Hypolimnetic Mass Balance of Mercury from a Dimictic Lake: Results from the METAALICUS Project. 12th International Conference on Heavy Metals in the Environment. Grenoble, France. May 26-30, 2003.
  - Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft, T. R. Trinko, M.T. Tate. Towards a Hypolimnetic Mass Balance: Results from the Mercury Experiment to Assess Atmospheric Loading In Canada and the United States (METAALICUS). Experimental Lakes Area, Canadian Dept of Fisheries and Oceans. June 24, 2003.
  - Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft. Early results from the mercury experiment to assess atmospheric loading in Canada and the United States. Environmental Chemistry & Technology Program, University of Wisconsin. September 19, 2003.
  - Babiarz, C.L., S.P. Chadwick, J.P. Hurley, D.P. Krabbenhoft, T. R. Trinko, M.T. Tate. Towards a Hypolimnetic Mass Balance: Results from the Mercury Experiment to Assess Atmospheric

Loading In Canada and the United States (METAALICUS). 26th Midwest Environmental Chemistry Workshop. Iowa City, Iowa. October 10-12, 2003.

Report Follows

Watershed Transport and Transformations of Atmospherically Derived Mercury: A Whole Ecosystem Amendment Study

James P. Hurley, University of Wisconsin Water Resources Institute, David P. Krabbenhoft, US Geological Survey, Kristofer R. Rolfhus, University of Wisconsin

Problem and Research Objectives

Fish consumption advisories have been issued in US 40 states and all provinces of Canada, due to deleterious health effects associated with ingesting fish of high Hg concentrations. Nearly all of the mercury in fish is methylmercury (MMHg), a neurotoxin that biomagnifies to high concentrations toward the top of aquatic food webs. Small quantities of methylmercury in the diet can adversely affect wildlife and humans. Human and wildlife exposure to methylmercury is almost entirely through the consumption of fish. Thus, the greatest present research need is to further understand what drives this widespread contamination problem and to unravel the complex set of processes that link non-point mercury loading to bioaccumulation in fish.

There is a general consensus that, in the absence of direct point-source discharges, the primary source of Hg that bioaccumulates to upper trophic levels is atmospheric deposition. The U.S. EPA's Science Advisory Board identified in The Mercury Report to Congress (EPA 1997) several gaps regarding our current understanding of Hg cycling. In particular, they pointed to ecosystem cycling of atmospherically derived Hg, including post-depositional transport pathways, rates of transport, and biogeochemical transformation processes (methylation/demethylation and reduction/evasion).

Watershed characteristics (such as land cover patterns, soil type and glacial deposits) exert a strong influence on export, partitioning and speciation of Hg_T and MMHg from watersheds. These characteristics directly affect the types and amounts of suspended particulate matter (SPM), colloids, forms of DOC, and other ligands transported within and from terrestrial portions of catchments to down-gradient aquatic ecosystems where bioaccumulation of Hg in the food web begins. Elucidating the connections between atmospheric Hg loading and various watershed components (forest soils and vegetation, bedrock, wetlands, streams and lakes) and bioaccumulation in the food web is the general scope of the Mercury Experiment to Assess Atmospheric Loading in Canada and the U.S. (METAALICUS) project.

METAALICUS is a large, multidisciplinary, multi-investigator project, with an anticipated four-year budget totaling approximately nine million dollars (including the purchase of isotopes). The project is a whole-watershed application of stable-Hg isotopes at the Experimental Lakes Area (ELA), near Kenora, Ontario. The ELA is one of the very few places where direct application of contaminants in field studies is allowable, and emphasizes the unique opportunity that this study provides.

Overall objectives of the METAALICUS project are to:

1.Provide direct information on the effects of non-point atmospheric Hg deposition on bioaccumulation in predatory fish

2. Determine the relative importance of the watershed (including upland and wetland portions) and direct deposition in determining bioaccumulation of Hg in predatory fish of a lacustrine environment.
3. Provide (for the first time) direct measurement of ecosystem response times between Hg deposition and transport, and provide a direct comparison of the reactivity of Hg added via "new deposition" and Hg considered as the historic pool within the watershed.
4. To more definitively trace Hg processes and pathways at the ecosystem scale using near-ambient levels of isotopes.
5. Provide information on rates and pathways of Hg cycling to support a watershed-based Hg cycling model

Objectives for University of Wisconsin-USGS Subproject of METAALICUS

Because METAALICUS is a large project, principal investigators have been assigned various focus areas to ensure complete coverage of the major Hg transformation and transport studies. The investigators associated with our subproject will be specifically addressing upland and wetland Hg-cycling processes and pathways that contribute to Hg accumulation in aquatic food webs. Our efforts within this subproject support overall objectives 2 through 5 above.

Our objectives for this subproject are to:
1. Determine the fraction of a watershed Hg yield that is "new" versus that derived from the historic pool of Hg in the soils and vegetation.
2. Provide direct observations of the extent of mobility of new Hg in upland soils and wetland peat.
3. Isolate and quantify transport vectors (dissolved organic carbon, colloids, particulates) leading to export from different watershed components.
4. Assess the effects of partitioning and pathway in influencing bioavailability of Hg derived from uplands and wetlands to the study lake.
5. Elucidate the contribution of new versus historic Hg to the formation and optimal locations for methylation of Hg and relative mobility for transport from the watershed to the lake.

Methodology

The experimental design consists of both loading and tracer experiments. Mercury has an ideal distribution of stable isotopes that are all readily available from specialized distributors. We will increase Hg loads using 95% pure stable (non-radioactive) isotope of mercury [e.g., $^{199}Hg(NO_3)_2$, $^{200}Hg(NO_3)_2$, $^{202}Hg(NO_3)_2$] using the techniques in Hintelmann et al. 1995 and Hintelmann and Evans 1997. The spike will be delivered to upland/wetland plots and mesocosms by diluting the mercury isotope into rainfall collected on site. During full-scale ecosystem addition of spike-equilibrated water, we will add separate isotopes to the upland, wetland and lake components of the watershed. The use of enriched stable isotopes of Hg allows for the analytical discrimination of new "labeled" Hg and background Hg at trace concentrations. Ratios of isotopic Hg to ambient Hg in the same samples can be analyzed to determine the relative availability of "old" versus new Hg inputs. Isotopic Hg can also be used to follow Hg through different watershed transformation and transport processes and subsequently through different compartments of the lacustrine food web.

During both pilot scale and full-scale implementation, we will use physical and chemical fractionation techniques (developed at the University of Wisconsin) to describe the composition and chemical lability of organic-Hg complexes in runoff and wetland discharge. These methods serve to separate aqueous Hg species by size and their ability to form complexes with competing solid phase ligands attached to resins, creating both concentrated ligand and ligand-free test solutions. Ultrafiltration methods will characterize the importance of sub-particulate fractions (colloids and truly dissolved species) to the transport and bioavailability of upland and wetland Hg. For example, we have observed that inorganic Hg in the <100 kD fraction of inundated ELA forest soil extracts are the most readily available for uptake to aquatic bacteria, using the *mer-lux* bioreporter assay (K. Scott, pers. comm.). The Chelex studies allow for kinetic and thermodynamic evaluation of Hg binding strength and reactivity, and directly addresses whether weakly-bound Hg complexes are biogeochemically important. The XAD treatments will further characterize the organic ligands to which Hg is bound, including hydrophobicity, acidity, and molecular weight. We will also be conducting reactive Hg measurements to operationally determine chemical lability of Hg-DOC fractions.

This project utilizes the cooperative efforts of the University of Wisconsin Water Chemistry Program (UWWCP) Mercury Laboratory and the USGS Mercury Research Laboratory (both in Madison, Wisconsin). Groups at both laboratories have specialized facilities and instrumentation for trace metal research. Each laboratory has dedicated clean room facilities developed for low-level Hg processing and analysis. The UWWCP facility has three Hg analytical systems (Tekran, Brooks-Rand) as well as supporting instrumentation such as a Perkin-Elmer Plasma II ICP-OES; Waters 600 HPLC with 991 Diode Array Detector; PE 5100Z GFAA; Shimadzu TOC-500 with a particulate carbon analyzer. Modern shop facilities located in our UW building allows for fabrication of specialized equipment. The USGS facility houses the main instrumentation for isotopic analyses for this study, a new Perkin-Elmer Elan 6000 that is dedicated for mercury-only isotopic analysis. In addition, the USGS lab has four Tekran Hg analytical systems, and an OI TOC-1010 carbon analyzer.

Principal Findings and Significance

Phase 1 of METAALICUS involved pilot studies and baseline work in 2000 while Phase 2 is the full scale additions scheduled to begin in June 2001. The pilot studies are yielding fundamental new information about the cycling of mercury in terrestrial and aquatic ecosystems. For example, in 1999, we added 12.5 µg/m^2 of ^{202}HgII to a wetland plot, approximately doubling the annual mercury deposition rate of mercury at the ELA. The isotopic mercury was much more mobile than expected, penetrating into the 10-20 cm below the peat surface. In 1999, we also added 12.5 ug/m2 of ^{202}HgII to a 680m^2 upland catchment at the ELA. Over the first growing season, only about 8% of the ^{202}HgII was lost to the atmosphere, and only 0.3% of the ^{202}HgII was exported from the upland catchment. In 2000, we also added ^{200}HgII to the upland and wetland plots and to four 10-meter diameter lake enclosures. Preliminary results from the enclosures demonstrate loss of ^{200}HgII to the atmosphere, and rapid movement of ^{200}HgII to the periphyton on the sediment surface and walls of the enclosure, but minimal movement into sediments.

Our group also participated in characterization of Hg dynamics in Lake 658, the lake of the planned isotopic watershed/lake addition, to prepare for full-scale addition studies. Intense

monitoring of the lake and the zone of the sediment-water interface were characterized in order to predict the response of added isotope within the lake. We observed trends in increasing dissolved organic carbon and total Hg in Lake 658 in response to rainfall runoff from both the upland and wetland. We also observed intense recycling of Hg and MeHg at the sediment-water interface in response to deposition of freshly-deposited material settled from the epilimnion.